CHAPTER 1

INTRODUCTION

1.0 INTRODUCTION

Petroleum coke is a solid byproduct of petroleum refining, useful in the production of electrodes used as carbon anodes for the aluminum industry, graphite electrodes for steel making, as fuel in the firing of solid fuel boilers used to generate electricity, and as fuel for cement kilns. Malaysia produces a very high percentage of all petroleum coke, and coking capacity continues to increase (Roskill Consulting Group, 1999.).

Petroleum coke is of increasing importance in the cement industry, and is growing in use within the electricity generating and industrial boiler communities as well. Further, as utilities shift their focus towards lower cost generation including solid fuel supercritical boilers and continue to investigate integrated gasification-combined cycle combustion turbine (IGCC) generating stations, petroleum coke will continue to grow in importance as a solid fuel.

There are several petroleum based opportunity fuels led by petroleum coke. These fuels have made their way into large utility and industrial boilers, and into process industries such as cement manufacture and steel production. The characteristics of petroleum coke indicate a fuel that is high in calorific value and carbon content, however it is not highly reactive as indicated either by maximum volatile yield, H/C atomic ratio, O/C atomic ratio, or the kinetics of devolatilization and char oxidation.

1.1 Project Background

Petroleum coke (petcoke) is a black colored solid produced by the high pressure thermal decomposition of heavy or high boiling petroleum process streams and residues. Calcined petroleum coke has lower volatile matter, higher percentage of elemental carbon and lower potential for toxicity (William D.Callister, 2003).

Petcoke high calorific value and low price has offered economic conversion to many commercial fuel users especially in high-cost generating facilities. The attractiveness of fuel grade petcoke extends beyond price characteristics. The typical heat content is high (>32.68 MJ/kg or 14,000 Btu/lb) and low ash content (typically <1 percent ash). Many have reviewed the concept of blending the petcoke with firing fuel to further reduce fuel costs. By increasing the percentage of petcoke in the blended fuel, average fuel cost is further reduced. However, there are concerns about high percentage of petcoke creating combustion problems such as fouling or plugging of the boiler convection pass because of its low volatility (Narula, 2002).

As a result of alternative energy research, petcoke is found to be the most potential source for power generating. It is higher in potential and meeting the challenges of increasing energy demand and pollutant gases emission. There is extensive utilization to process heat in the endothermic steam gasification of petcoke to synthesis gas. Such fossil processes were used for H_2 production in order to generate electricity in fuel cells, as well as the generation of CH_4 as a gaseous fuel (Awalludin, 2009).

1.1.1 Solid Fuel

Solid fuel refers to various types of solid material that are used as fuel to produce energy and provide heating, usually released through combustion. Solid fuels have long been used by humanity to create fire. The use of some solid fuels is restricted or prohibited in some urban areas, due to unsafe levels of toxic emissions. The use of other solid fuels such as wood is increasing as heating technology and the availability of good quality fuel improves. In some areas, smokeless coal is often the only solid fuel used.

Nowadays, solid fuels such as biomass, coal and soils are developed by using various techniques but public law is taken into account. The use of water slurry solid fuel reduces the emission of dangerous gases. They are also treated with various solutions under the research programs in order to improve the safety of the fuel.

1.2 Problem Statement

Petcoke is primarily used in the making of carbon anodes for aluminum industry. Since it is insloluble honeycomb material that is the end product of thermal processes, the development is very limited (Speight, Proximate Analysis, 2005). The use of coke as a fuel is hampered by its high sulfur and metals content making it less suitable for conventional combustors. Therefore there is a need to study a process of converting to a more suitable fuel normally in form of solids, slurries of gases. The heavy metals constituents were present in the petcoke in concentrations of about 100 to 5,000 ppm or more (Schlinger, 1971). These metal constituents or their reaction products were found to attack the refractory lining, causing equipment failure and shutdowns.

The composition of petcoke is generally complex; contain large amounts of high molecular weight complex hydrocarbons and rich in carbon but correspondingly poor in hydrogen. The molecular composition is also varies with the source of crude oil, and in this study, varies after the nitration at various temperatures. In addition to carbon, hydrogen, and metallic constituents, it also contains considerable amounts of NO_x and SO_x that must be determined before sale or use. So, there is a need of an experiment to determine its composition.

The density (specific gravity) of petcoke has a strong influence on its future use. Since there is a variation of petcoke origins, the real density can be different for different batches of petcoke. However, there is a possibility that these calcined cokes might be able to produce a water dispersible solid fuel after undergoing a certain treatment. That way, the application of calcined cokes can be developed.

1.3 Objectives and Scope of Study

The objectives of the present project are to study the calorific values of petcoke as per received from PETRONAS Penapisan Melaka (PPM) after being nitrated at 50^{o}C, 75^{o}C and 95^{o}C by mean of its chemical and physical properties and to study on the calorific values of the mentioned petcoke to be used as fuel in the burner or gasifier. This study also aimed on a study on suitability of the mentioned petcoke to be used as water dispersible solid fuel. There are a few parts on the scope of study which is a study of chemical and physical properties, a study on calorific values of local petcoke in Malaysia obtained from PPM also by means of its chemical and physical properties and a compatibility study of them The proximate and ultimate analyses are run simultaneously to characterize the slurry fuel.

Among the interesting parameters in the chemical analysis is energy content of the samples, CHONS content, calorific value, moisture, volatile matter, fixed carbon and ash content. The physical analysis would research into determining the bulk density value. The results from the present study can be applied for future study on a large scale utilization system. All these chemical and physical properties were compared among each of the petcoke samples to see the trend and potential of the samples according to each temperatures. The scope of work involved would be the reactions of PETRONAS cokes towards nitration process which later studied by using TGA, Spectrophotometry, CHNS and Bomb Calorimetry.

All of the findings will be recorded in the forms of tables, charts and plot of graphs to discuss the potential of PETRONAS Cokes to be used as water dispersible fuel. Statistical analyses will be done to study the feasibility of petcoke. Since there is a variation of petcoke properties, the data can be different for different nitration temperatures.

CHAPTER 2

LITERATURE REVIEW

2.0 LITERATURE REVIEW

In this chapter a review of the available literature on petroleum coke is represented. Some of the work on this topic is available upon studies being carried out for the time being.

2.1 Petroleum Cokes

Petroleum coke or petcoke, a refinery byproduct, has generally been considered as an unusable byproduct because of its high sulfur content. However energy industries now view petcoke as a potential feedstock for power generation because it has higher carbon content than other hydrocarbons like coal, biomass and sewage residue. This gives petcoke a great edge over other feed stocks to generate power, (Ramkumar, 2008). Petroleum coke is a byproduct of the coke drum in refinery process which upgrades fuel oil by heating it and cracking it to higher valued gasoline, jet and diesel components.

2.1.1 Origin of Petroleum Cokes

Cokes originated from crude oil. Crude oil is the term for "unprocessed" oil, the stuff that comes out of the ground. It is also known as petroleum. Crude oil is a fossil fuel, meaning that it was made naturally from decaying plants and animals living in ancient seas millions of years ago. Because crude oil is made up of a mixture of hydrocarbons, this first and basic refining process is aimed at separating the crude oil into its "fractions," the broad categories of its component hydrocarbons.

Crude oil is heated and put into a still-a distillation column- and different products boil off and can be recovered at different temperatures. The lighter products; liquid petroleum gases (LPG), naphtha, and so-called "straight run" gasoline are recovered at the lowest temperatures. Middle distillates; jet fuel, kerosene, distillates (such as home heating oil and diesel fuel) come next. Finally, the heaviest products (residuum or residual fuel oil) are recovered, sometimes at temperatures over 1000 degrees F. This is where the cokes come from. The simplest refineries stop at this point.

2.1.2 Types of Cokes and its Applications

The various types of coke are generally used for specific applications. Green coke can be prepared by different processes and as a consequence may be described as delayed process coke, fluid process coke or flexicoke. The green coke must have sufficiently low metals content in order to be used as anode material. Green coke with this low metals content is referred to as anode grade coke.

Green coke is the primary solid carbonization product from high boiling hydrocarbon fractions obtained at temperatures below 900 K. It contains a fraction of matter that can be released as volatiles during subsequent heat treatment at temperatures up to approximately 1600 K. This mass fraction, the so-called volatile matter, is in the case of green coke between 4 and 15 weight percent, but it depends also on the heating rate. Green Coke may contain up to 15% residual hydrocarbon. The green coke with too high metals content will not be calcined and is used for burning. This green coke is called fuel grade coke (Wikipedia.com).

Calcined petroleum coke (CPC) is the product from calcining petroleum coke. Calcined coke is produced by heating green coke to temperatures up to 1200°C. .The calcined petroleum coke is used to make anodes for the aluminium, steel and titanium smelting industry. Generally there is lower ash (<0.5%), lower moisture (8-10%) and lower Volatiles (8-10%) than steam coal, resulting in a much higher heating value, on the order of 14,000 Btu/lb. There is generally higher sulfur, ranging from about 4 % to 7 %, while the HGI varies from 35 to 75. Needle coke for instance is calcined and then used in the production of electrodes due to its lower electrical resistivity and coefficient of thermal expansion.

Petroleum coke is increasingly being used as full or partial placement for coal in electrical power generation. The blending of coke with coal, in appropriate proportions, allows for environmental emission compliance and improves ignition and flame stability. Fluidized bed combustion is commonly used to burn petroleum coke. Gasification is increasingly used with this feedstock (often using gasifiers placed in the refineries themselves).

Most coke produced is fuel grade, meaning it competes with coal. Some coke is very low in Iron, Nickel and Vanadium, thereby achieving a higher value in the aluminum anode industry. V and Ni (chemically bonded) and Na (dissolve as sodium chloride in water which is entrained with a crude oil) catalyzed anode oxidation accelerating anode consumption and are ingot impurities (Jun Lee, *et. al*., 1997).

Production costs associated with petcoke are minimal because it is a byproduct of the refining process, and prices are generally determined by the competitive steam coal price. Pricing is also generally discounted to compensate for sulfur, HGI and the extra difficulties of the end user managing both coal and coke inputs.

Presently, there is about 60 million tons/yr of coke produced worldwide, most of it located at coastal refineries in North and South America. In a few years it will be close to 70 million tons/yr as new refineries with cokers are being built in the US, Mexico and Venezuela. Since the Americas are generally coal exporters, most of this coke is also exported to the same areas that consume imported steam coal: primarily Japan and Europe.

Cement plants and power plants are the 2 greatest consumers of pet coke. There is some limited use as space heating and in commercial brick kilns in Europe, and a small but emerging market for met coal blending component for the steel industry. While the higher sulfur may limit the coke in a coal/petcoke blend in a plant designed for coal, more recently designed Circulating Fluidized Bed (CFB) boilers can burn 100% high sulfur coke (Ramkumar, 2008).

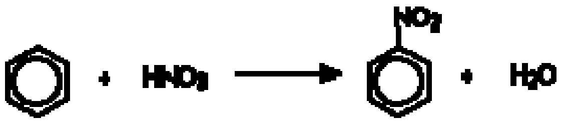
2.2 Nitration Effect on Hydrocarbons

Nitration is one of the oldest and the most extensively studied reactions. Moreover, this process has been the most acceptable and famous route for the manufacture of explosives, precursors for dyes and intermediates, and industrial solvents. The nitro group was introduced in the organic matrix of hydrocarbon via oxidative nitration, using dilute nitric acid. An effect of nitration towards petroleum coke is de-ashing. There are indications that are of the possibility of removing ash from carbonaceous material by treating them with nitric acid. Oxidization causes coal organic matter solubilization. The total amount of hydrogen diminishes through the removal of aromatic hydrogen in nitration.

An example of nitration is shown below using benzene as the hydrocarbon. Nitration happens when one (or more) of the hydrogen atoms on the benzene ring is replaced by a nitro group, NO_2.The experimental results reveal that introduction of the nitro group substantially enhanced the solubilization of hydrocarbon in aqueous organic solvents. The study reveals that the nitro groups present in oxynitrated hydrocarbons had an important role in solubilizing it in aqueous organic solvents (Debapriya, 2007).

The nitrated mesophase lost its original hydrophobicity and can be readily dispersed in distilled water and dissolve at high pH. The electrolytic and colloidal natures are due to the presence of hydrophilic ionizable groups introduced as a result of nitration.

Benzene is treated with a mixture of concentrated nitric acid and concentrated sulphuric acid at a temperature not exceeding 50°C. The mixture is held at this temperature for about half an hour. Yellow oily nitrobenzene is formed. The concentrated sulphuric acid is acting as a catalyst. The nitro group introduced to the compound enhanced the solubility of the hydrocarbon.



$$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$$

Figure 2.1: Nitration of benzene

The role of the NO_2 group is of utmost importance, with respect to hydrocarbon solubilization in aqueous organic solvents. Previous research has proved that calcined coke can be water dispersible after treating with nitration. The properties of the calcined coked also did improve after nitration (Hidayah, 2009).

The earlier studies on the oxidation of coke use air, permanganate, nitric acid, trifluoroacetic acid−hydrogen peroxide, and performic acid have been performed. These studies have suggested specific mechanisms of oxidative degradation, with respect to each type of oxidant. In the past, the oxidation of coal preceded using 16 N nitric acid, with an intent to produce aromatic polycarboxylic acid. Because the reaction is vigorous and nonspecific, much degradation occurred; this degradation was due to the severity of the reactions, and, therefore, solubility studies on coke/treated coal became difficult (Debapriya, 2007).

The use of nitric acids alone resulted in the formation of a large amount of complex oxidation products which on electrolysis remained in the center compartment, even in the presence of excess alkali (B. Juetter 1937).

2.3 Spectrophotometry

In physics, spectrophotometry is the quantifiable study of electromagnetic spectra. It is more specific than the general term electromagnetic spectroscopy in that spectrophotometry deals with visible light, near-ultraviolet, and near-infrared. Also, the term does not cover time-resolved spectroscopic techniques.

Spectrophotometry involves the use of a spectrophotometer. A spectrophotometer is a photometer (a device for measuring light intensity) that can measure intensity as a function of the color (or more specifically the wavelength) of light. Important features of spectrophotometers are spectral bandwidth and linear range of absorption measurement (Zhu, 2004).

Chemists commonly use absorbance spectroscopy, or how a substance absorbs photons of light, to obtain both qualitative (identity) and quantitative (amount) information. The quantitative measurement is achieved because each photon of light absorbed corresponds to the excitation of a single electron.

All spectrophotometer instruments designed to measure the absorption of radiant energy have the basic components as follows:

1. A stable source of radiant energy (Light);
2. A wavelength selector to isolate a desired wavelength from the source (filter or monochromator)
3. Transparent container (cuvette) for the sample and the blank;
4. A radiation detector (phototube) to convert the radiant energy received to a measurable signal; and a readout device that displays the signal from the detector.

The energy source is to provide a stable source of light radiation, whereas the wavelength selector permits separation of radiation of the desired wavelength from other radiation. Light radiation passes through a glass container with sample. The detector measures the energy after it has passed through the sample.

The readout device calculates the amount of light absorbed by the sample displays the signal from the detector as absorbance or transmission. The spectrophotometers which are used for such measurements may vary from simple and relatively inexpensive colorimeters to highly sophisticated and expensive instruments that automatically scan the ability of a solution to absorb radiation over a wide range of wavelengths and record the results of these measurements. (http://www.rrcap.unep.org)

In this project, the stability of the dispersion of the colloid will be determined as time increase using spectrophotometer. A spectrophotometer is a machine which operates on the principle of Beer-Lambert's Law; that is: the absorbed light is directly proportional to the concentration of the solution while the transmitted light is inversely proportional; the darker the solution, the more concentrated it is.

Figure 2.2: Spectrophotometer used in Chemical Laboratory

2.4 Test Parameters

There are a few important parameters in this project that can be summarized in the table below:

Table 2.1: Testing parameters in the project.

Parameters	**Description**
Moisture content	The quantity of water in the material, express as a percentage of the material's weight. Higher moisture contents reduce the thermal efficiency of the burner and results in low gas heating values
Volatile Matter	Refers to the part of the petcoke that is released when the petcoke is heated up from 400°C to 900°C. Fuel with high volatile matter content produces more tar and lead to problems.
Ash content	A mineral content of fuel which remains in oxidized form after combustion of fuel. Melting and agglomeration of ashes in reactor causes slagging and clinker formation.
Elemental Composition	High carbon content would highlight the possibility of the petcoke samples to become a fuel source for the gasification process. Low sulfur content would portray the potential of the petcokeas an environmental friendly.
Calorific Values	Obtained in most cases in an adiabatic, constant volume bomb calorimeter. Fuel with higher energy content is always better for gasification.

Apart from these, the bulk density is also tested using a method which will be discussed later in the methodology part. The methodology part also covers the specific activities which have been carried out such as proximate analysis, ultimate analysis and density analysis.

2.4.1 Moisture Content

Water can be found in petcoke. There are high percentages of water both physically and chemically bound. This water is still present at various stages of coking process. Many petcoke are washed with water during preparation and subjected to rain during transportation and storage. The total moisture in petcoke is the determination of the moisture that resides within the matrix. It ranges from 2-5% by weight. The standard methods of determining the amount of moisture in petcoke include variety of test methods designed to differentiate it from other coke and coals (ASTM D-1412).

2.4.2 Volatile Matter

Volatile matter, as determined by the standard test methods (ASTM D-3175), is the percentage of volatile products, exclusive of moisture vapor, released during the heating of coal or coke under rigidly controlled conditions. The measured weight loss of the sample corrected for moisture establishes the amount of material (volatile matter) evolved from the petcoke under the conditions of the test. However, the method, being empirical, requires close adherence to detailed specifications, and since the test is essentially an assay of the sample of petcoke on a small scale rather than a purely chemical test, it is necessary in order that results may be comparable among laboratories that the conditions prescribed be followed rigidly.

2.4.3 Ash Content

Ash is the residue remaining after the combustion of petcoke under specified conditions (ASTM D3174) and is composed primarily of oxides and sulfates. It is always be confused with mineral matter, which is composed of the unaltered inorganic minerals in petcoke (Given and Yarzab, 1978). Thus ash is formed as the result of chemical changes that take place in the mineral matter during the ashing process. The quantity of ash can be more than, equal to, or less than the quantity of mineral matter in petcoke, depending on the nature of the mineral matter and the chemical changes that take place in ashing. Several formulas have been proposed for calculating the amount of mineral matter originally in the petcoke using data from ashing techniques as the basis of the calculations. Using the Parr formula mineral matter content of petcoke is derived from the expression:

$$\text{Mineral matter (\% w/w)} = 1.08A + 0.55S \qquad \textbf{(Eq 2.1)}$$

Where A is the percentage of ash in the petcoke and S is the total sulfur in petcoke.

2.4.4 Elemental Composition

The composition of petcoke is very complex. Therefore in this study it only involves determination of the weight percent of carbon, hydrogen, nitrogen, sulfur (CHNS) as well as oxygen (usually estimated by difference. Trace elements that occur in petcoke are often included as part of the ultimate analysis.

Carbon and hydrogen, which, respectively, account for 70 to 95% and 2 to 6% by weight (dry, ash-free) of the organic substance of petcoke, are thought by some to be the most important constituents of petcoke. Almost all of the carbon and hydrogen in petcoke occurs in combined form in the complex organic compounds that make up petcoke. But carbon also occurs in the mineral carbonates and hydrogen is also present in the various forms of moisture found in petcoke. It is important that accurate determinations be made and appropriate corrections for overlapping values, especially hydrogen, be calculated. Thus the oxygen content,

$$O = 100 - (C + H + N + S + \text{ash}) \qquad \textbf{(Eq 2.2)}$$

All values are expressed as percentages and C is the as-determined carbon (ASTM D-3178), H is the as-determined hydrogen (ASTM D-3178), N is the as-determined nitrogen (ASTM D-3179), S is the as-determined sulfur (ASTM D-3177; ASTM D-4239), and “ash” is the as-determined ash (ASTM D-3174).

2.4.5 Calorific Values of Petroleum Cokes

The calorific value is the heat produced by the combustion of a unit quantity of petcoke in a bomb calorimeter with oxygen and under a specified set of conditions (ASTM D-121; ASTM D-2015; ASTM D-3286). For the analysis of petcoke, the calorific value is determined in a bomb calorimeter by an adiabatic method with a correction made if net calorific value is of interest. The unit is calories per gram, which may be converted to the alternate units (1.0 kcal/kg = 1.8 Btu/lb = 4.187 kJ/kg).

The calorific value is a direct indication of the heat content (energy value) of the petcoke and represents the combined heats of combustion of the carbon, hydrogen, nitrogen, and sulfur in the organic matter and of the sulfur in pyrite and is the gross calorific value with a correction applied if the net calorific value is of interest. The calorific value is usually expressed as the gross calorific value (GCV) or the higher heating value (HHV) and the net calorific value (NCV) or lower calorific value (LHV).

The calorific value of petcoke is an important property. For example, the gross calorific value can be used to compute the total calorific content of the quantity of coal or coke represented by the sample for payment purposes. It can also be used to compute the calorific value versus sulfur content to determine whether the petcoke meets regulatory requirements for industrial fuels. The gross calorific value can be used to evaluate the effectiveness of beneficiation processes. Finally, the gross calorific value can be required to classify coal or coke (ASTM D-388). The energy content of the petcoke can be expressed as the useful heating value (UHV), which is an expression derived from the ash and moisture contents through the formula:

$$\text{UHV (kcal/kg)} = 8900 - 138 \times [\text{ash content (wt \%)} + \text{moisture content (wt \%)}] \quad \textbf{(Eq. 2.3)}$$

It is also possible to make a close estimation of the calorific value (CV) by using formulas (Selvig, 1945):

1. The Dulong formula:

   $$CV = 144.4(\%C) + 610.2(\%H) - 65.9(\%O) - 0.39(\%O) \quad \textbf{(Eq. 2.4)}$$

2. the Dulong-Berthelot formula:

   $$CV = 81.370 + 345\,[(\%H - (\%O + \%N - 1)) / 8)] + 22.2(\%S) \quad \textbf{(Eq 2.5)}$$

Where %C, %H, %N, %O and %S are the respective carbon, hydrogen, nitrogen, oxygen and organic sulfur contents of the petcoke.

CHAPTER 3
METHODOLOGY

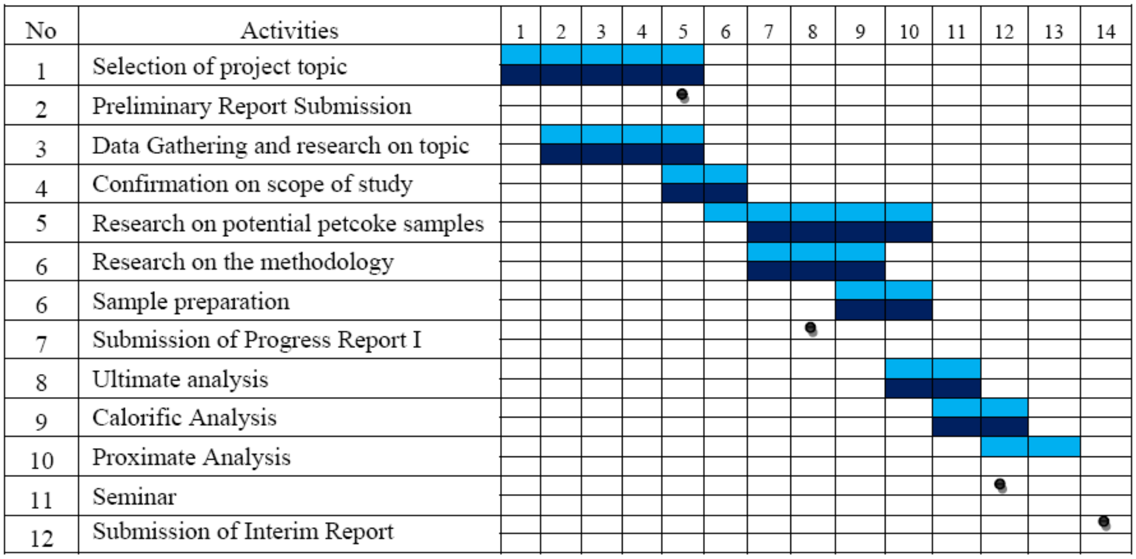
3.0 METHODOLOGY

The calorific values of PETRONAS cokes nitrated at 50°C, 75°C and 95°C not only include simple calculations using formulas and testing using bomb calorimeter, but it also include the determination of its physical and chemical analyses. The basic parameters needed to calculate the calorific values using formula are mentioned in the literature review.

For the first half of the semester the samples are investigated under Proximate Analysis after nitration process at the various temperatures above. The samples are petroleum cokes obtained from PETRONAS refinery plant. The nitrated samples are then further investigated under TGA, and Spectrophotometer to investigate the suitability as water dispersible solid fuel. The second half of the study is the Ultimate Analysis or chemical analysis, density analysis and the calorific test using CHNS Analyzer and Bomb Calorimeter respectively. The results of both period of study are recorded and the data obtained are used to investigate the calorific values of the samples.

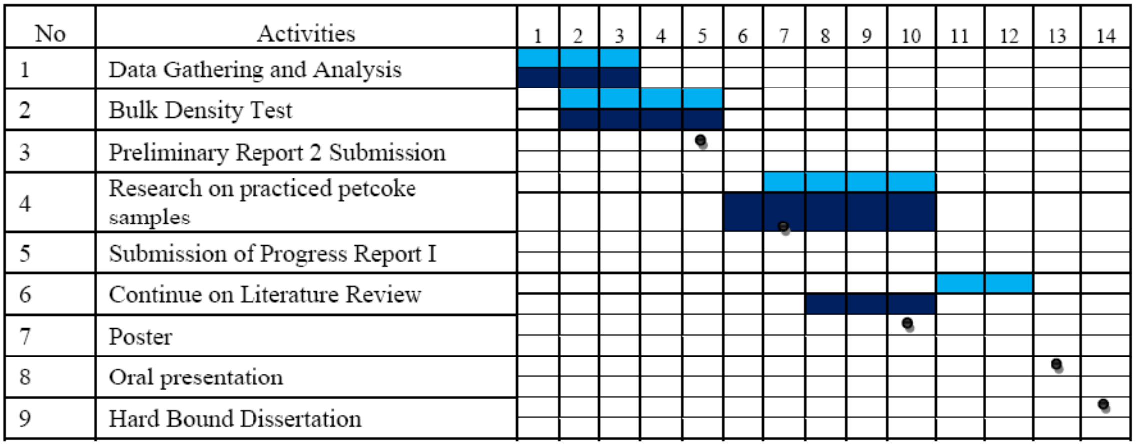
All the tests and study done are using the equipments provided in the university with the guidance and support from the lab technologists, project supervisors and others. Given sufficient time and funds, the study of calorific values of PETRONAS cokes nitrated at 50°C, 75°C and 95°C would be further investigated by using estimation analysis by using formulas and repeat the proximate and ultimate test as many as possible to ensure good repeatability and reproducibility result. All the safety measures are taken as stated by the equipment standard operation procedures (SOP) and the material safety data sheets (MSDS) prepared prior to conducting the experiments.

The research work took up a 2 academic semester period to complete the project. As mentioned in Chapter 1, research methodology is based on nitration process, characterization and properties tests. The project's Gantt charts are shown in Figure 3.1 and 3.2.



No	Activities	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of project topic	🟦 ⬛	🟦 ⬛	🟦 ⬛	🟦 ⬛	🟦 ⬛									
2	Preliminary Report Submission					●									
3	Data Gathering and research on topic		🟦 ⬛	🟦 ⬛	🟦 ⬛	🟦 ⬛									
4	Confirmation on scope of study					🟦 ⬛	🟦 ⬛								
5	Research on potential petcoke samples						🟦	🟦 ⬛	🟦 ⬛	🟦 ⬛	🟦 ⬛				
6	Research on the methodology							🟦 ⬛	🟦 ⬛	🟦 ⬛					
6	Sample preparation									🟦 ⬛	🟦 ⬛				
7	Submission of Progress Report I								●						
8	Ultimate analysis										🟦 ⬛	🟦 ⬛			
9	Calorific Analysis											🟦 ⬛	🟦 ⬛		
10	Proximate Analysis												🟦	🟦	
11	Seminar												●		
12	Submission of Interim Report														●

Figure 3.1: Gantt chart for Semester 1



No	Activities	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Data Gathering and Analysis	🟦 ⬛	🟦 ⬛	🟦 ⬛											
2	Bulk Density Test		🟦 ⬛	🟦 ⬛	🟦 ⬛	🟦 ⬛									
3	Preliminary Report 2 Submission					●									
4	Research on practiced petcoke samples						⬛	🟦 ⬛	🟦 ⬛	🟦 ⬛	🟦 ⬛				
5	Submission of Progress Report I							●							
6	Continue on Literature Review								⬛	⬛	⬛	🟦	🟦		
7	Poster										●				
8	Oral presentation													●	
9	Hard Bound Dissertation														●

Figure 3.2: Gantt chart for Semester 2

3.1 Analysis Considerations

The calorific values of petcoke are associated with other properties that are expressed in term of numerical values resulting from a few chronological tests. There is a requirement that reliable standard test method to be applied to petcoke analyses. The results from the test methods used must be in the recognized range of error of the experimental procedure so that the numerical data can be fixed values and not just approximations.

Table 3.1: Test properties and results descriptions

Test/Property	Results/Comments
Sample history	Sampling date, type, origin (coking location)
Proximate analysis/Chemical properties	Determination of the "approximate" overall composition (i.e, moisture, volatile matter, ash and fixed carbon content)
Ultimate analysis/Empirical formulation	Absolute measurement of the elemental composition (i.e, carbon, hydrogen, sulfur, nitrogen, and oxygen content)
Bulk density test/bulk density	Measurement of the true density of samples
Calorific test/Heat of combustion	Measurement of the heat of combustion

The analyses are reported on a few bases with regard to moisture and ash content. Results are *as-determined* refer to the moisture condition of the petcoke samples during the analyses in the laboratory. There is also air-dry samples meaning that the samples are brought with moisture content approximately equilibrium with laboratory atmosphere, (std. temperature and pressure). *As-received* basis is the moisture condition when the sample arrived in the laboratory. To obtain this basis, gain or loss of weight during air drying is determined. There is also a basis called *as-sampled* basis which is no gain or loss of moisture occurs. In order to retain the moisture, the samples are sealed in plastic containers. If no moisture associated with the sample, analyses can be reported on a *dry basis.* The moisture value is used for base conversion from as determined data to the dry basis. *Dry,ash free basis* data are calculated on the assumption that there are no moisture and mineral matter associated with the sample. The data is determined from moisture and ash determination are used for the conversion and determining the moisture capacity or known as equilibrium moisture.

These factors apply to calorific values as well as to proximate and ultimate analysis. The conversion factors of components other than hydrogen and oxygen is given in the table below.

Table 3.2: Conversion factors of components other than hydrogen and oxygen

Given	**As-determined (ad)**	**As-received (ar)**	**Dry (d)**	**Dry Ash-free (daf)**
As-determined (ad)	-	$\frac{100-M_{ar}}{100-M_{ad}}$	$\frac{100}{(100-M_{ar})}$	$\frac{100}{(100-M_{ad}-A_{ad})}$
As-received (ar)	$\frac{100-M_{ad}}{100-M_{ar}}$	-	$\frac{100}{(100-M_{ar})}$	$\frac{100}{(100-M_{ar}-A_{ar})}$
Dry (d)	$\frac{100-M_{ad}}{100}$	$\frac{100-M_{ar}}{100}$	-	$\frac{100}{(100-A_{d})}$
Dry Ash-free (daf)	$\frac{100-M_{ad}-A_{ad}}{100}$	$\frac{100-M_{ar}-A_{ar}}{100}$	$\frac{100-A_{d}}{100}$	-

M, percent moisture by weight; A, percent ash by weight. For example, given ad, to find ar, use the formula

$$ar = ad \times (100-M_{ar}) / (100-M_{ad}) \qquad \textbf{(Eq3.1)}$$

3.1.1 Sample History

The sample is petroleum coke, obtained from PETRONAS refinery plant. The coke is taken from the coke drum of the plant.

Table 3.3 Major Equipments of Unit 32-1 Delayed Coker Unit (PPM)

EQ. No	Description	Des.Press/Temp	Opr. Press/Temp	Dimension
V-32201/2	Coke Drums	4.2 - 7.4 kg/cm^{2}g / 516 - 504^{o}C	1.8 - 2.8 kg/cm^{2}g/ 446 - 499^{o}C	8.2 x 22 m (Dia x TT)
EQ. No	Description	Capacity	Type	No of Burners
F-32201	Delayed Coker Furnace	34.8 MW	Double Fired, Four Passes, Air Pre-Heater, Horizontal Tubes	128 (32 per cell)
EQ. No	Description	Capacity	Disc. Pressure	Type
P-32271	Decoking Jet Water Pump	227 M^3/H	229 kg/cm^{2}g	Centrifugal Multi-Stage
EQ. No	Description	Dimension	Des. Temp & press	Internals
C-32201	Coker Main Fractionator	3.5 X 45.6 m (I.D x TT)	343 - 454^{o}C & 3.5 /FV	40 Valve Trays

The coke drum (V-32201/2) operated for a minimum 2 years without major shutdown. It has cycle time of 20 hrs. The design pressure and temperature are 4.2 - 7.4 kg/cm^{2}g and 516 - 504^{o}C respectively. The operating pressure and temperature are 1.8 - 2.8 kg/cm^{2}g/ 446 - 499^{o}C respectively with dimension of 8.2 x 22 m. The simplified process flow diagram (PFD) of the unit is included in the appendices. (PPM)

The petroleum cokes were obtain by lump and let dry under the sun for a period of 3 days to ensure a dry sample. The samples were further dried in electric oven at 55^{o}C for a period of 24 hours. This will eliminate the pre-treatment moisture on the petcoke.

The dried petcoke are undergone grinding in order to make powder form using a Granulator. The granulated petcoke are then pulverized into the powdery form using a Rock Lab Grinder. The time is set 5 minutes per load.

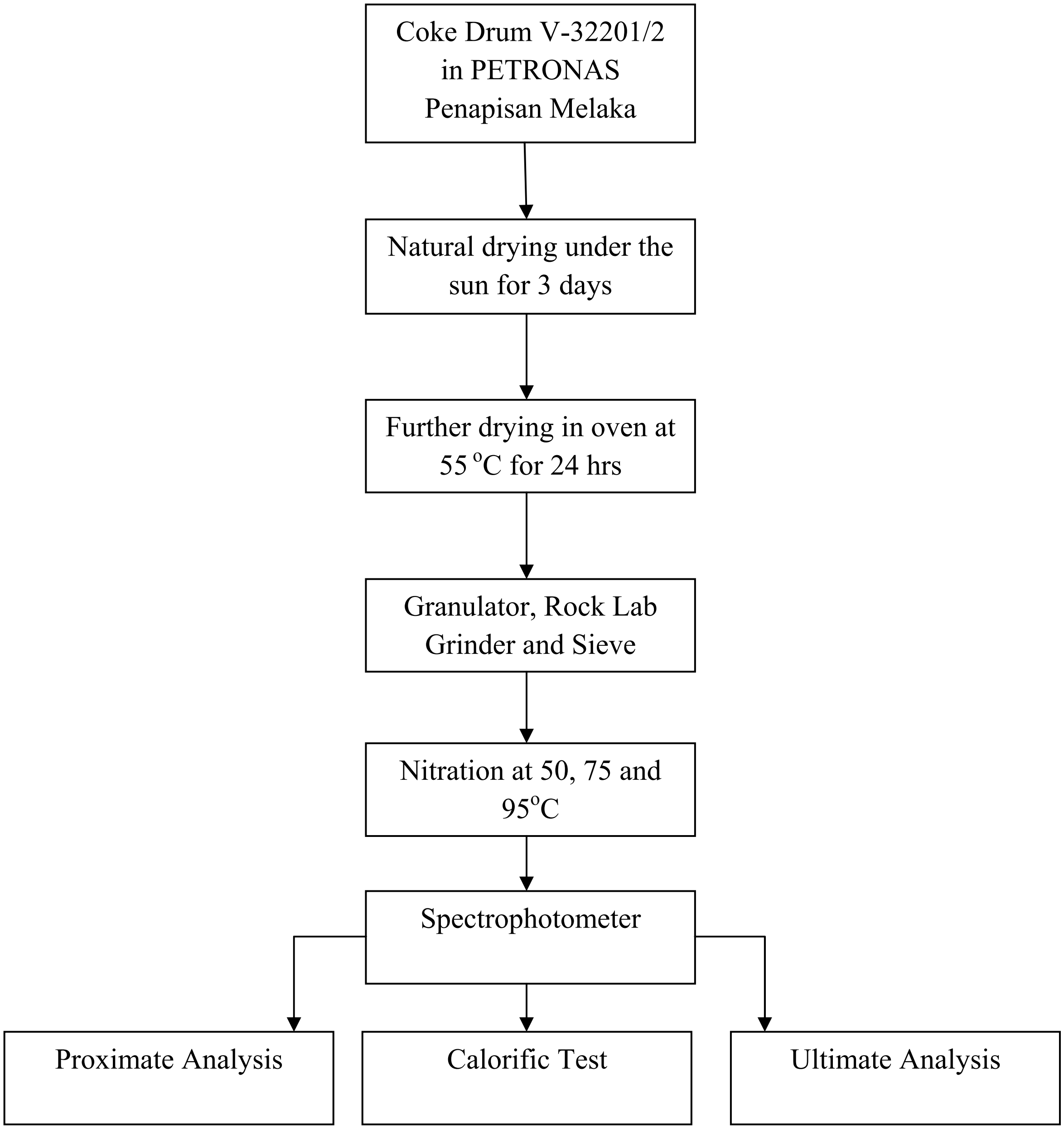


Figure 3.3: Methodology

3.2 Nitration of PETRONAS Cokes at 50, 75 and 95^{o}C and Spectrophotometry

During the nitration process, three samples of calcined coke are treated with nitration at three different temperatures which are 50, 75 and 95^{o}C. These three samples of calcined coke along with the reference sample of calcined coke (untreated calcined coke) then underwent parameter testing which are FTIR Analysis and also Thermo Gravimetric Analysis. From the results gained, the analysis is done. After thorough analysis and discussion, then only the project concluded whether it's successful or not.

Apparatus:

1. Nitric Acid & Concentrated Sulfuric acid
2. Petroleum coke
3. Beaker
4. Stirrer/Glass rod
5. Thermometer
6. Heater
7. Filter
8. Hydrochloric Acid
9. Oven
10. Fume Cupboard
11. Distilled Water
12. Gloves

Procedure:

1. 12.5 g of pulverized petroleum cokes were added in small amount at a time into a reaction set up containing 250 mL of concentrated sulphuric and nitric acids.
2. The mixture were cooled down using a water bath while constant stirring were applied until the evolution of reddish brown gaseous nitric acid was about to stop.
3. The mixture then heated for 5 hrs at different temperature ie. 50, 75 and 95^{o}C with constant stirring.
4. The mixture then cooled to room temperature while maintaining the agitation and the nitrogen (optional) flow overnight.
5. The reaction mixture was then poured into 1250 cm^3 distilled water, filtered and washed with a continuous flow of distilled water until filtrate gave pH > 4.
6. The filtrate also checked for product in the solution by treating it with concentrated HCI solution.
7. The wet, nitrated petroleum coke weighed and then dried using oven at 60^{o}C. (Bambang Ariwahjoedi,Ph Thesis). The visualization of the nitration process is presented in the Figure 3.4 -3.9.

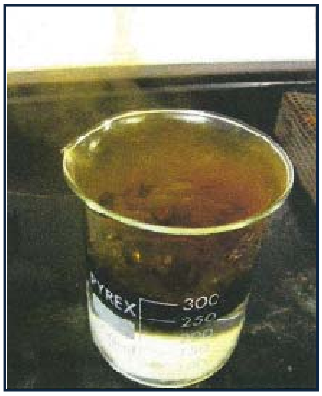


Figure 3.4

Reddish brown gaseous evolved when concentrated $HN0_2$ + H_2S0_4 mixed with Calcined coke

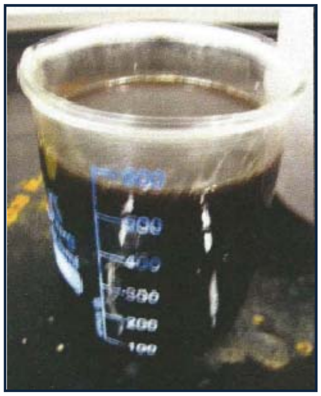


Figure 3.5

After 5 hours of heating, the mixture-color changed to black

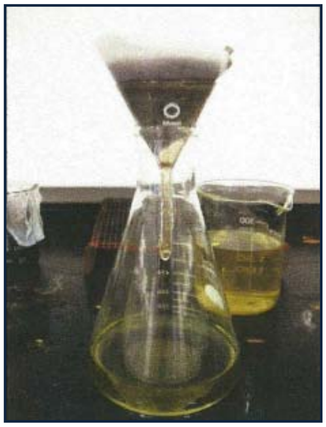


Figure 3.6

The mixture filtered to separate the nitrated Calcined coke from the solution

Figure 3.7

Wet nitrated calcined coke

Figure 3.8

The remaining solution in a beaker

Figure 3.9

The nitrated calcined coke after baked in the oven

Three types of nitrated cokes were prepared earlier at 3 difference temperatures which are at 50^{o}C, 75^{o}C and 95^{o}C is examined in this experimental work. The sulfuric acid was acting as a catalyst. It also absorbed water. The resulted nitrated cokes then were used to find the maximum absorption wavelength. The Beer's Law plot was applied in order to get the maximum absorption.

After the maximum absorption wavelength was defined using the UV-Vis spectrophotometer, those 3 types of nitrated cokes at different temperature were weighted each 0.002gram before mixed with 20 ml of buffer solution at pH of 4,7 and 10. Then, using the spectrophotometer again the absorbance is recorded versus time. All the characteristic of the dissolve or dispersed coke in buffer solution is observed and analyzed. The pattern of the graph obtained was then further discussed.

In order to differentiate and verify the setting rate of the petcokes to settle down in buffer solution of pH 4 and pH 7, the 3 nitrated cokes were analyzed again. The settlement time is recorded by letting it 'free falling' in a test tube for a certain time and the time was measured. In this case, the test is not done for pH 10 since the nitrated petcokes dissolved totally in alkaline solution. The data obtain was analyzed and discussed.

The tools, hardware and chemicals involved in this experiment are Spectophotometer, Gloves, Stirrer/ Glass Rod, Beaker, Thermometer, Stop watch, Test Tube, Fume cupboard, Concentrated Nitric acid, Concentrated Sulfuric Acid, Buffer solution of pH 4, pH 7 and pH 10, calcined petroleum coke nitrated at 3 difference temperatures which are at 50^{o}C, 75^{o}C and 95^{o}C. Standard laboratory procedure must be followed. Safety glasses must be worn during this experiment.

3.3 Proximate Analysis

Proximate analysis is to be carried out to determine the percentage of moisture, volatile matter, fixed carbon and ashes in the petcoke. Proximate analysis is an empirical technique in which the mass of substance is heated at a controlled rate and the mass loss is recorded as a function of time. The parameters of Thermo Gravimetric Analysis were set based on ASTM E 1131-98, Standard Test Method for Compositional Analysis by Thermogravimetry. The basic principle of a TGA analysis module is to record mass loss during programmed time or temperature profile. Changes in mass indicate moisture loss and phase changes which occur at set temperature indicative of the compound. It can be used to determine water of crystallization, follow degradation of materials, determined reaction kinetics, study oxidation and reduction.

Procedure:

1. Hold the sample for 1 min at 500^{o}C
2. Heat from 50^{o}C to 110^{o}C at 60^{o}C/min
3. Hold for 5 min at 110^{o}C
4. Heat from 110 to 800^{o}C at 100^{o}C/min
5. Old for 3 min at 800^{o}C
6. Heat from 800^{o}C to 900^{o}C at 200^{o}C/min
7. Hold for 5 min at 900^{o}C

Fuel with moisture content above about 30% makes ignition difficult and reduces the CV of the product gas due to the need to evaporate the additional moisture before combustion/gasification can occur (Mckendry, 2001). High moisture content reduces the temperature achieved in the oxidation zone resulting in the incomplete cracking of the hydrocarbons released from the pyrolysis zone.

3.4 Ultimate Analysis

The purpose of preparing a fine dry power is to analyze the chemical compositions of the petcoke. The ultimate analysis or CHNS testing was performed using the Leco CHNS-932 machine. The CHNS machine works based on the principle that high temperature combustion is used as the means of removing the elements from the material. This analysis will report the (carbon, hydrogen, nitrogen, and sulfur) content in the coke samples. The products of combustion in the CHNS analysis are CO_2, H_2O, N_2, and SO_X. The gases, which are carried through the system by the helium carrier, are swept through the oxidation tube packed with either tungsten trioxide (which adds oxygen) or copper sticks (which removes oxygen), to complete the conversion to SO_2. The H_2O is swept through the non-dispersive infrared absorption detection system where it is measured, Anhydrone then removes the H_2O and the remaining gases are swept through the SO_2 and CO_2. Lecosorb and Anhydrone leaving the helium carrier gas and N_2 remove the CO_2 and the H_2O. The N_2 is measured by thermal conductivity. Adjustments for blank, calibration, and weights are applied to the final integrated signal and the answers are displayed as weight percent carbon, hydrogen, nitrogen and sulfur.

The parameter for ultimate analysis was set according to ASTM D 3176-89. The weight that would be used for the test would be 1mg in form of fine powder. A set of 5 runs would be conducted to obtain an average value for the composition of each Carbon, Hydrogen, Nitrogen and Sulfur in the palm cokes. High carbon content would highlight the possibility of the petcoke to become a fuel source for the gasification process. Low sulfur content would portray the potential of the palm cokes as an environmental friendly renewable energy source as sulfur would and react with water, oxygen and oxidants to form acidic compound as found in acid rains.

Procedure:

1. Samples need to be ensured in the powder form.
2. One capsule is taken and weighted. The weight value at weight machine is tare.

Picture of capsule can be referred in Figure 3.10

3. One type of sample is selected and put in the capsule. The weight of the capsule fill with sample is weighted.

NOTE: To weight of the sample is estimated between 0.5- 1 gram.

4. Capsule is compacted until there is no more air inside.

NOTE: All works deal with capsule cannot be handled by hand.

5. Step 1 to 4 is the repeated to other samples.
6. All samples are then placed in the machine. The weight value for each sample is entered in the machine.
7. Start the experiment as the all the weight value is entered.
8. Experiment takes approximately 20 minutes for each sample. The reading of Carbon, Hydrogen, Nitrogen and Sulfur content for each sample is taken after experiment is finished.

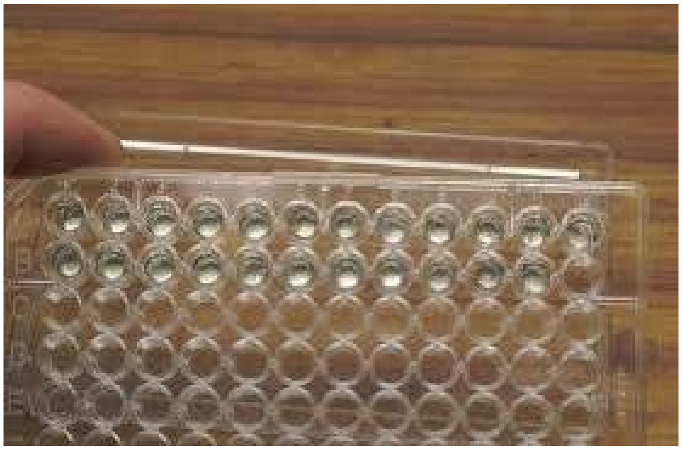


Figure 3.10: Capsule used in CHNS analysis

3.5 Calorific Test

To determine the amount of energy stored in the petcoke samples, a Calorific Value Test would be done using a LECO AC-350 Bomb Calorimeter. The bomb calorimeter is the most common device for measuring the heat of combustion or calorific value of a material. The basic principles behind bomb calorimeter are:

1. Supply oxygen to the sample to ensure it burns completely
2. Burn the sample quickly so that the heat produced has little time to diffuse into the surrounding environment before measuring the total change in the water temperature
3. Enclose the reaction inside a strong chamber to contain the high pressure of the rapidly-burning sample

Gross Calorific value of a fuel specimen is the heat produced by a complete combustion of a unit quantity of sample, at a constant volume, in an oxygen bomb calorimeter under standard condition. The parameter for the calorific test was done according to ASTM D 5865-07, Standard test Method for Gross Calorific Value of Coal and Coke. The test would be a judging parameter on the suitability or potential of the nitrated cokes by means of comparing the value of data obtained against the predetermined existing data of untreated coke. A set of 5 runs would be conducted to determine the average energy value contained in calcined petroleum coke nitrated at 3 difference temperatures which are at 50^{o}C, 75^{o}C and 95^{o}C in units of kJ/kg.

Procedure:

1. Machine is turn on and wait to be stabled
2. Ceramic Bowl is weighted and the weight value at weight machine is tare.
3. While waiting for machine to stable, samples can be prepared. Take one type of sample and place some amount of them into a ceramic bowl. The ceramic bowl with samples is then weighted. The amount of samples in ceramic bowl is then

adjusted so that the weight of the sample between 5 to 10gram. The final reading of sample weight is taken.

4. The thread is then tight to wire connecting the two conductors as shown in figure 3.4. The ceramic bowl is placed on its sit and the thread is then need to be buried inside into the sample.
5. The bomb conductor is then placed into its container and locked.
6. The Bomb is then tightened into the bomb sit. Wait until the machines give a 'Ready' signal. Start button is pushed to start the experiment.

NOTE: Experiment takes approximately 30 minutes for each sample.

7. Then the experiment is finished, the bomb is unlocked and opened. All the area in the bomb needs to be cleaned and dried.

CAUTION: Release the pressure inside the bomb before open by pushing the release valve

8. Reading of Higher Heating Value of the samples is taken
9. Step 2 to 8 is repeated for the other samples

Figure 3.11 below shows the schematic diagram for bomb calorimeter experiment set-up:

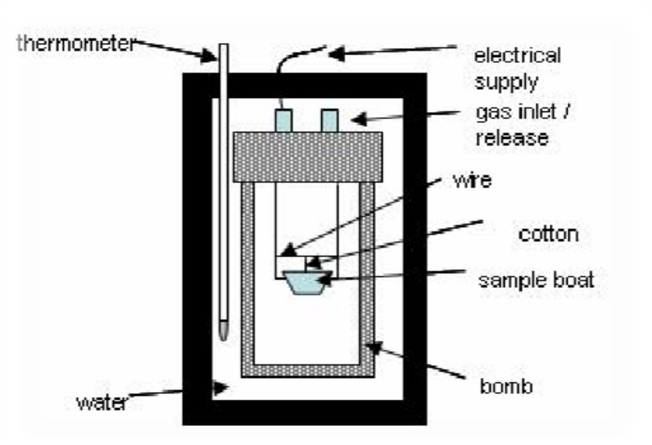


Figure 3.11: Schematic Diagram for Bomb Calorimeter (Eco-Beach Project, 2008)

3.5 Bulk Density Test

An important characteristic of solid fuel is their bulk density. Bulk density is defined as the weight per unit volume of loosely fuel. Fuels with high bulk density are advantageous because they represent a high energy-for-volume value. These fuels need less bunker space for a given refueling time. Inadequate bulk densities can be improved by briquetting or pelletizing. The bulk density of the petcoke is determined by measuring the sample weight with a lab scale for W1 and W2 and measuring its volume using Archimedes principle as shown in Figure 3.12 below. The sample was drenched in water and the displacement volume was measured using a lab measuring cylinder. Five tests were conducted to assess the repeatability of the results.

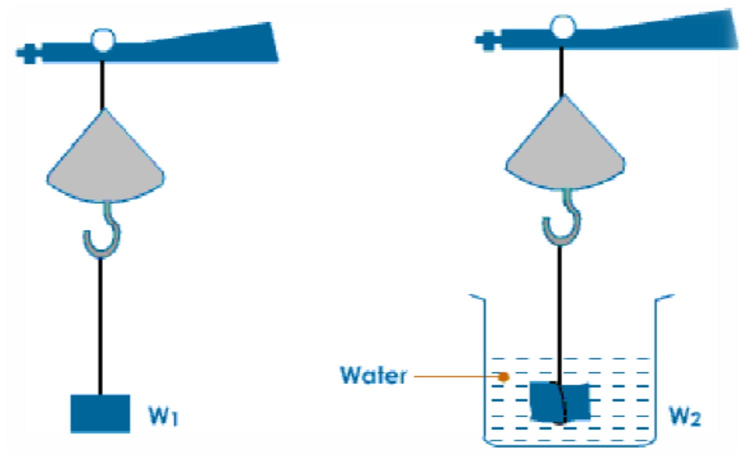


Figure 2.12 Experiment set up for the bulk density value test.

CHAPTER 4

RESULTS AND DISCUSSION

4.0 RESULTS AND DISCUSSION

This chapter will discuss the results obtained by the work discussed in Chapter 3. The data is presented in the form of tables, charts and plots of graph. The detailed interpretation and justification for each result are included with the data. However, the detail calculations are only done for the value of the first row of the data and the remaining (average calculations) are added in the appendices.

4.1 Proximate Analysis

Proximate analysis was carried out as procedure in the methodology with an average sample weight of 12.03mg. The parameters of TGA analysis were set based on ASTM E 1131-98. A typical proximate analysis graph is shown in Figure 4.1 below.

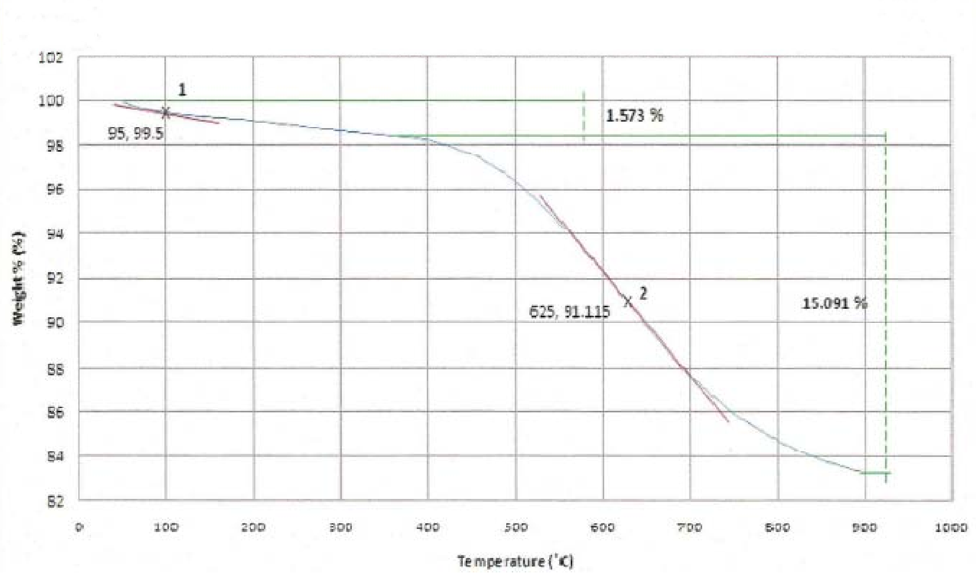


Figure 3.1: A typical proximate analysis graph obtained for sample of PETRONAS Cokes

The weight percentage of moisture, volatile matter, fixed carbon and ashes in the PETRONAS cokes nitrated at 50°C, 75°C and 95°C are presented in Table 4.1 below:

Table 4.1 Weight Percentage of Volatile Matter, Fixed carbon & Ash of the Calcined Coke Sample

Sample	Moisture / Volatile Mater (wt %)	Fixed Carbon (wt %)	Ash (wt %)
Reference	1.573	15.091	-
50 °C Nitrated Coke	7.554	29.437	21.063
75 °C Nitrated Coke	7.147	29.252	20.835
95 °C Nitrated Coke	6.565	27.578	20.966

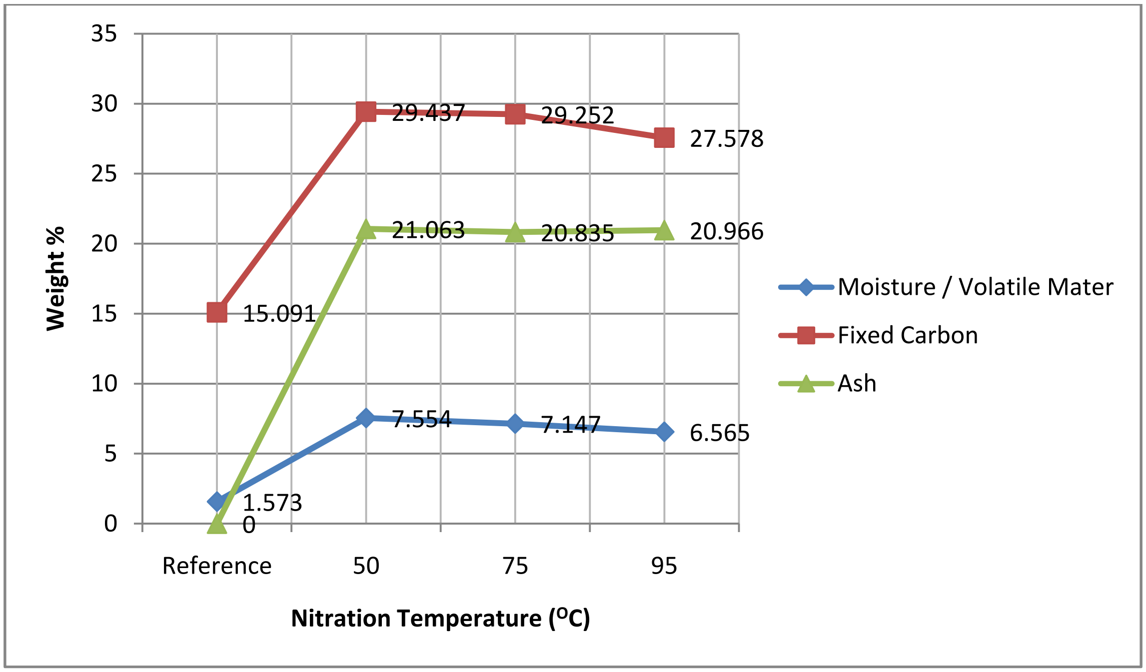


Figure 4.2: Graph of Weight Percentage of Volatile Matter, Fixed carbon & Ash of the Nitrated Calcined Coke Sample

In the results shown in Figure 4.2, the amount of moisture and volatile matter can be added together because the study is only interested with the amount of fixed carbon and ash content. The highest values are represented by the coke that is nitrated at 50°C. The ash and fixed carbon are the highest, 29.437 % and 21.063 % respectively. The gain of carbon and ash are 14.346% and 21.063% respectively.

4.2 Ultimate Analysis

The ultimate analysis or CHNS testing was performed using the Leco CHNS-932 machine. The result of the analysis is as shown in Table 4.2.

Table 4.2: Experimental Result of CHNS Test.

Nitration Temperature °C	Element	C %w	H %w	N %w	S %w
Reference coke	Reading1	30.56	3.055	0.658	1.834
	Reading2	23.91	-0.037	0.403	1.652
	Reading3	40.67	6.571	0.941	3.686
	Average	31.71	3.20	0.67	2.69
	Standard Deviation	8.44	3.31	0.27	1.13
50	Reading1	64.92	2.603	7.157	4.657
	Reading2	60.68	2.543	6.996	4.371
	Reading3	60	2.678	7.104	4.369
	Average	61.87	2.61	7.09	4.47
	Standard Deviation	2.67	0.07	0.08	0.17
75	Reading1	53.98	2.777	7.14	4.888
	Reading2	53.73	2.486	6.738	4.009
	Reading3	54.86	2.679	6.874	4.2
	Average	54.19	2.65	6.92	4.37
	Standard Deviation	0.59	0.15	0.20	0.46
95	Reading1	54.02	2.569	7.034	3.647
	Reading2	52.33	2.431	6.75	3.572
	Reading3	51.41	2.42	6.596	3.467
	Average	52.59	2.47	6.69	3.56
	Standard Deviation	1.32	0.08	0.22	0.09

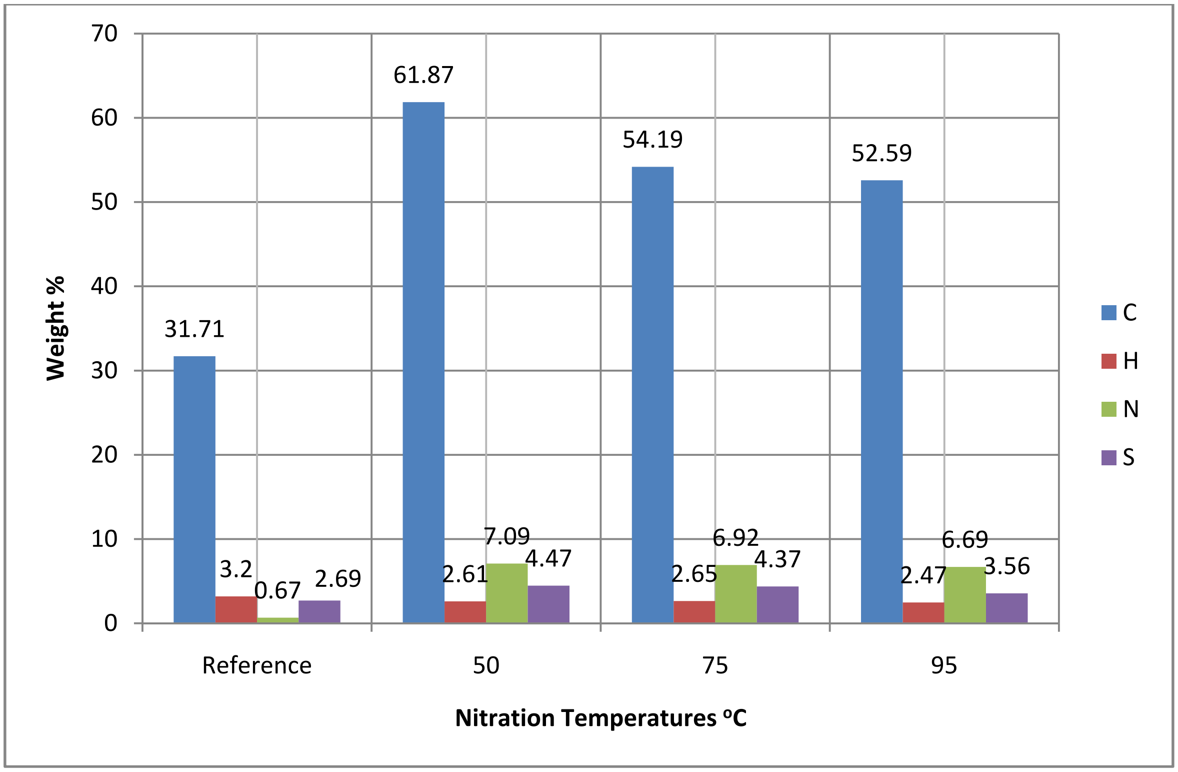


Figure 4.3: Ultimate Analysis for PETRONAS Cokes Nitrated at 50°C, 75°C and 95°C and Reference Coke

As shown in Figure 4.3, the average value of carbon obtained is at least 20.88% after the nitration. The highest carbon gain is 30.16% which are from 50°C nitrated coke.

4.3 Calorific Values Test Using Bomb Calorimeter

The calorific value of a material provides information regarding the energy content that maybe released when the referred material is burnt in air. The calorific value may be expressed both, as the higher heating value (HHV) and the lower heating value (LHV). The HHV may be defined as the total energy content released when the fuel is burnt in air, including the latent heat contained in the water vapor. It represents the maximum amount of energy potentially recoverable from a given biomass source. The LHV may be defined as the total energy content released when the fuel is burnt in air but excluding the latent heat contained in the water vapor. The result from the calorific test is shown in Table 4.3 to 4.6

Table 4.3: Experimental result of the Calorific test for Reference Coke

Test No.	Calorific Value, J/g
1	36100
2	35933
3	36153
4	36022
5	35991
6	36300
7	35753
8	36452
Average	36088
Standard Deviation	217.723284

Table 4.4: Experimental result of PETRONAS Cokes Nitrated at 50^{o}C

Test No.	Calorific Value, J/g
1	38204
2	39131
3	39671
4	40238
5	38762
6	38257
7	39750
8	41701
Average	39464.25
Standard Deviation	1157.33879

Table 4.5: Experimental result of PETRONAS Cokes Nitrated at 75°C

Test No.	Calorific Value, J/g
1	32081
2	33287
3	28917
4	32013
5	30014
6	28100
7	30046
8	28300
Average	30344.75
Standard Deviation	1923.96

Table 4.6: Experimental result of the PETRONAS Cokes Nitrated at 95°C

Test No.	Calorific Value, J/g
1	28732
2	27227
3	26200
4	18720
5	25190
6	30 650
7	18000
8	22541
Average	23801.43
Standard Deviation	4179.16

The calorific values of reference coke is quite high rand ranges from 35753 to 36452 J/g and the average is 36088 J/g which is very high compared to the calorific value for oil palm frond ranges from approximately 17933J/g to 18100J/g. This is because of the amount of carbon gain after the nitration increase the heat of combustion of the coke. For PETRONAS coke nitrated at 50°C, the range is from 38204 to 41701 J/g and the average is 39464.25 J/g. For PETRONAS coke nitrated at 75°C, the range is from 28100 to 33287 J/g and the average is 30344.75 J/g. For PETRONAS coke nitrated at 95°C, the range is from 18000 to 28732 J/g and the average is 23801.4286 J/g. This is because the value of carbon gain after nitration decreases as the nitration temperature increased. So, the most suitable treated coke is the one that nitrated at 50°C because of its high calorific value. The comparison of the calorific values for all samples is presented in Figure 4.4 below:

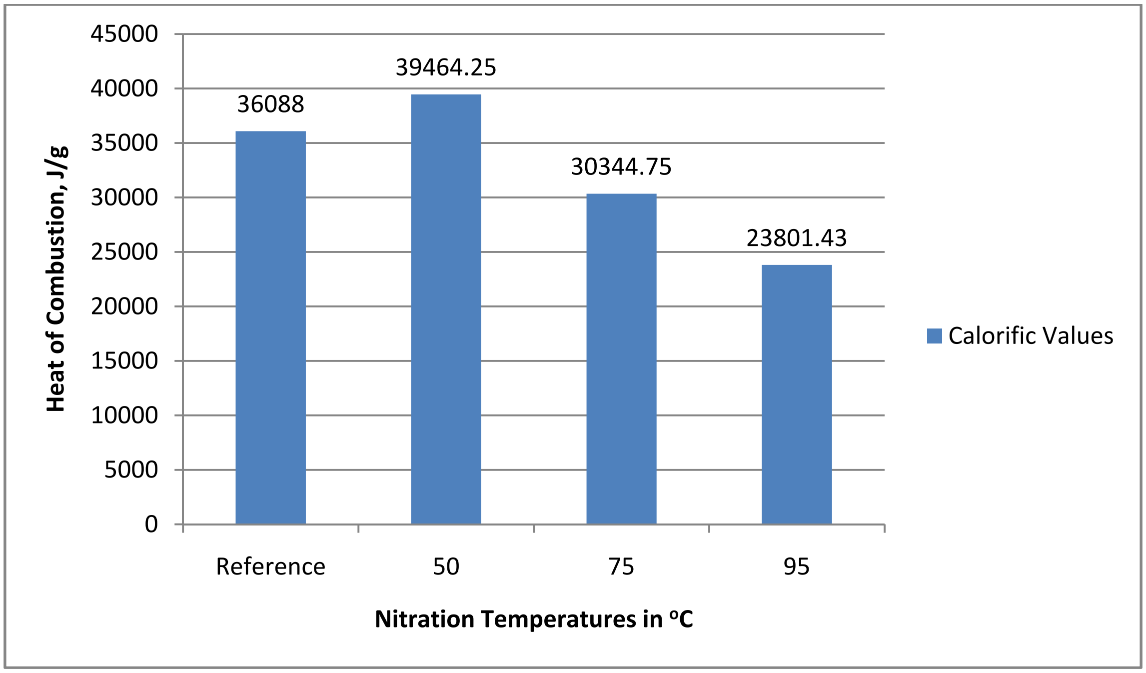


Figure 4.4 Comparison of the energy content of Nitrated PETRONAS Cokes against the Reference Coke

4.4 Bulk Density Test

Bulk density is defined as the weight per unit volume of loosely fuel. Fuels with high bulk density are advantageous because they represent a high energy-for-volume value. Table 4.7 shows the bulk density value obtained through measurement:

Table 4.7: Bulk density value from experiment of thw reference coke.

	Run 1	Run 2	Run 3	Run 4
Mass of sample, g	6.30	6.50	6.10	5.30
Displaced water volume, cm^3	4.70	4.90	4.50	3.80
Density, g/cm^3	1.34	1.33	1.36	1.39
Average density, g/ cm^3	1.35			
Standard Deviation, g/ cm^3	0.03			

Table 4.8: Bulk density value from experiment of PETRONAS Cokes Nitrated at 50°C

	Run 1	Run 2	Run 3	Run 4
Mass of sample, g	5.50	6.20	6.10	5.30
Displaced water volume, cm^3	6.20	7.20	6.90	6.20
Density, g/cm^3	0.89	0.86	0.88	0.85
Average density, g/ cm^3	0.87			
Standard Deviation, g/ cm^3	0.02			

Table 4.9: Bulk density value from experiment of PETRONAS Cokes Nitrated at 75°C

	Run 1	Run 2	Run 3	Run 4
Mass of sample, g	6.4	5.8	5.7	5.6
Displaced water volume, cm^3	6.2	6	5.3	5.5
Density, g/cm^3	1.03	0.97	1.08	1.02
Average density, g/ cm^3	1.02			
Standard Deviation, g/ cm^3	0.04			

Table 4.10: Bulk density value from experiment of PETRONAS Cokes Nitrated at 95°C

	Run 1	Run 2	Run 3	Run 4
Mass of sample, g	6.30	6.50	5.80	5.60
Displaced water volume, cm^3	6.20	6.00	5.30	5.20
Density, g/cm^3	1.02	1.08	1.09	1.08
Average density, g/cm^3	1.07			
Standard Deviation, g/cm^3	0.04			

The average bulk density value for PETRONAS Cokes Nitrated at 50, 75 and 95°C were determined to be 0.87, 1.02 and 1.07 g/cm^3 while the reference coke bulk density is 1.35 g/cm^3. The bulk density nitrated cokes are higher compared to other existing biomass fuels such as wood chips (0.230 g/cm^3), and straw (0.560 g/cm^3). A high bulk density value for PETRONAS nitrated cokes also indicates that the fuel will take less space for a given refueling time.

CHAPTER 5

CONCLUSION

The project has successfully met all its predetermined objectives to determine the calorific values of PETRONAS cokes nitrated at 50, 75 and 95^{o}C. From the chemical analysis, the carbon and sulfur content of the petcoke samples was determined to be 31.71% for the reference coke, 61.87%, 54.19% and 52.59% for PETRONAS cokes nitrated at 50, 75 and 95^{o}C respectively for carbon and 2.69% of reference coke, 4.47%, 4.43% and 3.56% for nitrated cokes at 50, 75 and 95^{o}C respectively for sulfur content. The calorific values are very high, 36088 J/g for reference coke, and 39464.25 J/g, 30344.75 J/g and 23801.4286 J/g for PETRONAS cokes nitrated at 50, 75 and 95^{o}C respectively. This proves the quantity of its energy is ready to be use as solid fuel. From the density test, the bulk density value of 1.35g/cm^3 of reference coke, 0.87g/cm^3, 1.02g/cm^3 and 1.07g/cm^3 for nitrated cokes at 50, 75 and 95^{o}C respectively shows a high energy-for-volume value. Exploiting the characteristic that it is readily available in abundant at a low cost, and taking into consideration the chemical and physical characteristic, it is justified that PETRONAS cokes nitrated at 50^{o}C are good to be used as water dispersible solid fuel.

For future works, PETRONAS Nitrated Cokes would be further investigated by nitrating at lower temperatures and constructing a burner to gain an understanding on the operational behavior of the cokes. It is hoped that the present research would provide a platform for future application of the project on large scale. A successful application of the present work on a large scale system would provide an alternative way to produce energy that is renewable and environmental friendly.

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APPENDICES

Appendix A: PETRONAS Cokes Nitrated at Various Temperatures Empirical Formula Calculation

Sample name	Sample mass/g	Carbon /mole	Hydrogen /mole	Oxygen /mole	Nitrogen /mole	Sulfur /mole
Reference Coke	100	2.64	3.17	3.88	0.05	0.07
50 DC Nitrated	100	5.15	2.59	0.18	0.51	0.14
75 DC Nitrated	100	4.51	2.63	0.69	0.49	0.14
95 DC Nitrated	100	4.38	2.45	0.85	0.48	0.11

Elements	Relative atomic mass
C	12.01
H	1.01
O	16.00
N	14.01
S	32.07

Samples	Empirical Formula
Reference unnitrated cokes	$C_{50}H_{44}O_{36}NS_2$
Nitration at 50, 75 and 95^{o}C	$C_{50}H_{24}O_{18}N_3S_2$

Error value for Calorific values from Bomb Calorimeter and Dulong Formula	
Reference unnitrated cokes	0.73
Nitration at 50^{o}C	0.76
Nitration at 75^{o}C	0.76
Nitration at 95^{o}C	0.79

Appendix B: Equipments Used in Proximate, Ultimate, Calorific Analysis and Sample Preparations

CHNS Analyzer

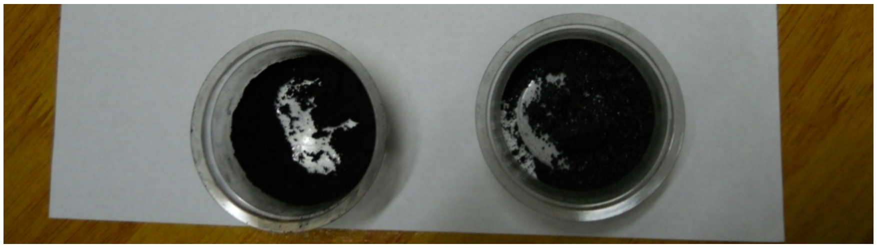
TGA

Oven

Granulator

Rock Lab Granulator (Crusher) **Bomb Calorimeter**

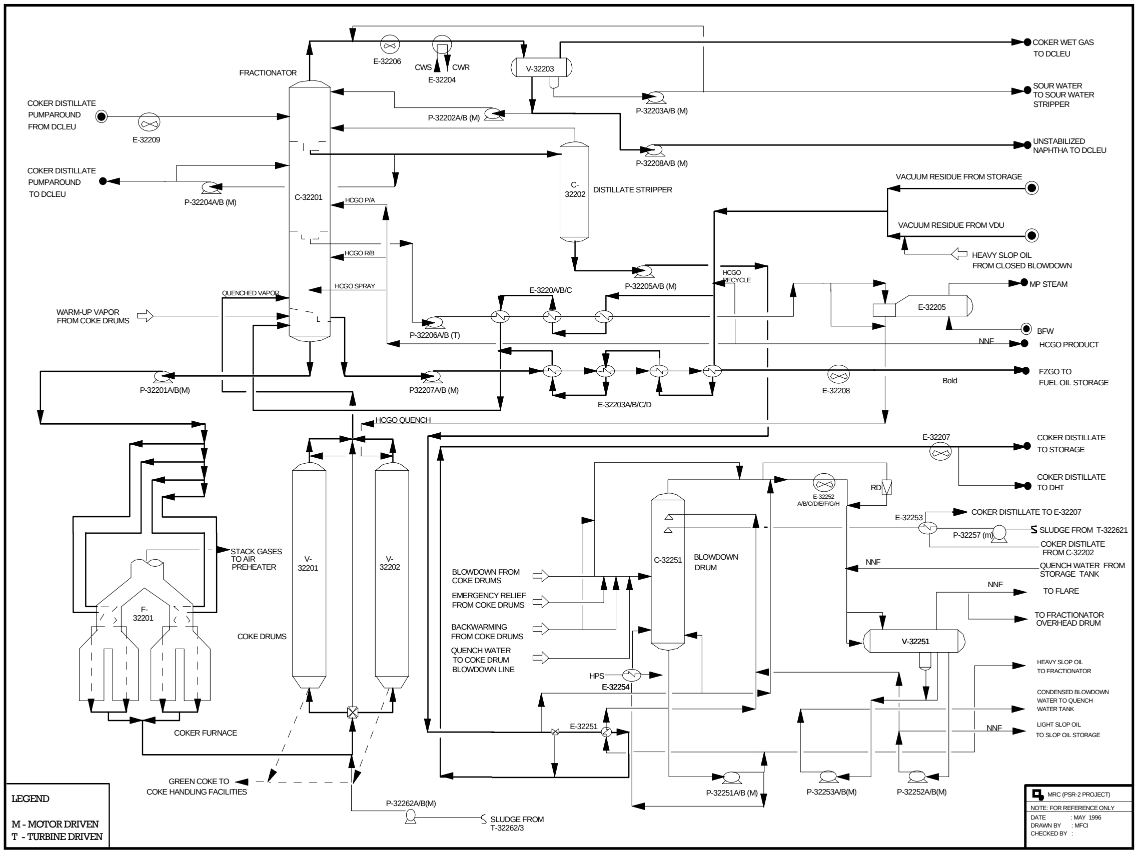
PETRONAS Coke Nitrated at 75^{o}C **PETRONAS Coke Nitrated at 95^{o}C**



PETRONAS Coke Nitrated at 50^{o}C **Reference PETRONAS Coke**

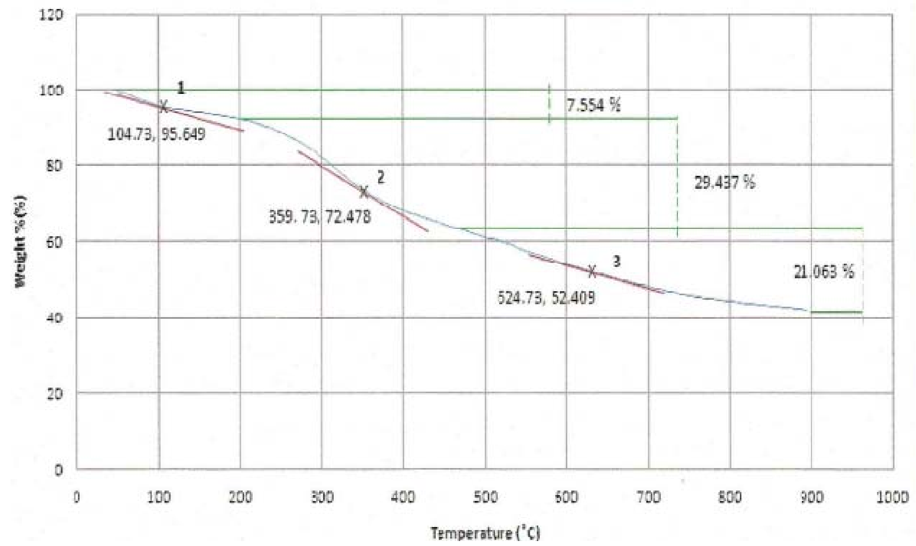
Appendix C: Coke Drum PFD

DELAYED COKER UNIT (32) - SIMPLIFIED FLOW DIAGRAM

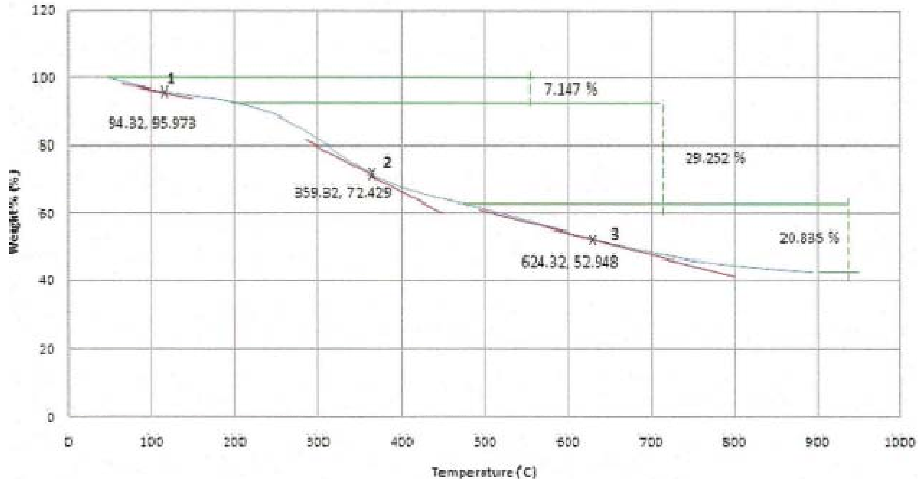


DISK BASIS DESIGN DRWG (B)/MFCI-DCU

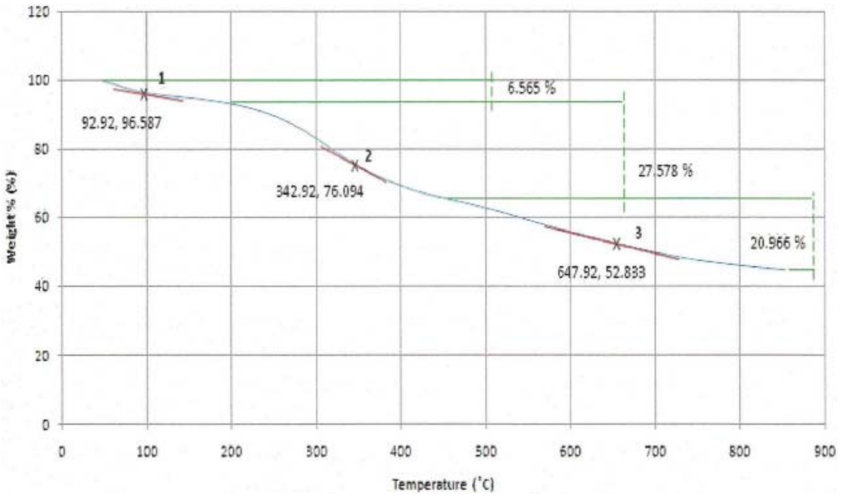
Appendix D: TGA Curves



Weight % vs Temperature Graph for Calcined Coke Nitrated at 50 ^{o}C



Weight % vs Temperature Graph for Calcined Coke Nitrated at 75 ^{o}C



Weight % vs Temperature Graph for Calcined Coke Nitrated at 95 °C

Proximate Analysis from the TGA Curves.

Sample	**Moisture / Volatile Mater (wt %)**	**Fixed Carbon (wt %)**	**Ash (wt %)**
Reference	1.573	15.091	-
50 °C Nitrated Coke	7.554	29.437	21.063
75 °C Nitrated Coke	7.147	29.252	20.835
95 °C Nitrated Coke	6.565	27.578	20.966